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THE LIFETIME OF AEROSOL DROPLETS IN AMBIENT AIR: CONSIDERATION OF THE EFFECTS OF SURFACTANTS AND CHEMICAL REACTIONS

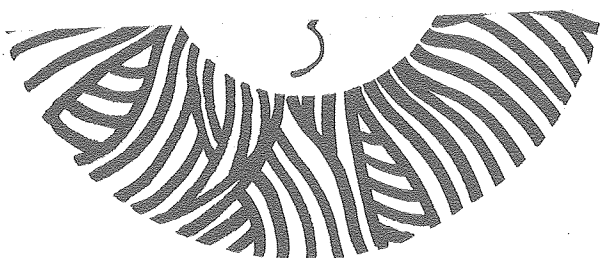R. Toossi and T. Novakov

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THE LIFETIME OF AEROSOL DROPLETS IN AMBIENT AIR:

CONSIDERATION OF THE EFFECTS OF SURFACTANTS AND CHEMICAL REACTIONS

R. Toossi and T. Novakov

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

The relatively long lifetime of droplets in atmospheric haze and fog in comparison to similar droplets of pure water is attributed to the presence of a monolayer of surfactant film and to the accumulation of soluble salts from chemical reactions. The lifetime of these droplets is a significant factor in the evaluation of the role of heterogeneous aqueous chemical reactions occurring in the troposphere. A new formulation is given which includes both these processes. As an example, the catalytic oxidation of SO_2 in the presence of liquid water droplets is investigated.

Introduction

The importance of chemical reactions involving liquid water droplets is well established (Beilke, 1978; Hegg, 1978; Middleton, 1980). The degree to which these reactions play a role in the atmospheric environment depends on the residence time of these droplets. There are indications that the lifetime of droplets in atmospheric haze and fog is considerably larger than the lifetime of pure water droplets of a similar size (Toossi, 1980). The chemical composition of these droplets is therefore an important factor in stabilizing atmospheric fog.

The lifetime of a droplet is enhanced at a given relative humidity by the presence of a film of surfactant material at the surface and by hygroscopic salt nuclei. The presence of the insoluble solid material enhances the effect of the soluble salt by increasing its concentration due to the smaller amount of water required to make a droplet of a given size and by acting as condensation surfaces for trace impurities. Cloud and fog samples collected by Kuroiwa (1955, 1951) and Ogiwara (1952) were found to contain just such soluble and insoluble particles, similar in nature, form, and size to haze and combustion-produced particles.

The kinetics of droplet evaporation is determined by factors which either change the equilibrium vapor pressure of the droplet or provide resistance to vapor and heat flow. Analytical solutions exist when either of these factors controls the rate of evaporation. For atmospheric aerosol droplets containing mixed nuclei of soluble and insoluble matter, both processes may be important in controlling the evaporation rate. In this paper we give a new formulation of the problem and investigate the effects of adsorption of the pollutant gases on the droplet surface and of the chemical reactions inside the droplet.

Mathematical Formulation

We assume that evaporation of the droplet proceeds by a two-step process —
1) the effusion of vapors through a vacuous boundary layer of thickness Δ, on
the order of the mean free path of evaporating molecules, and 2) by molecular
diffusion through the continuum (Fig. 1).   The rate of evaporation in a
vacuum is calculated from kinetic theory as (Fuchs, 1959; Bradley, 1955):

$$\frac{dm}{dt} = 4\pi r^2 \alpha (P'_r - P'_{r+\Delta}) \left(\frac{M}{2\pi RT}\right)^{1/2} , \tag{1}$$

where r is droplet radius, α is the vaporization constant, M is the molecular
weight, R is the gas constant, T is temperature, and m is the mass of evapora-
ting molecules. P'_r and $P'_{r+\Delta}$ are the partial pressure of vapor at the droplet
surface and at a distance Δ from the surface, respectively. Quasistationary
evaporation in a medium is controlled by the rate of diffusion of vapor to the
medium and conduction of latent heat of evaporation to the droplet. Assuming
small differences in the temperature between the droplet surface and the sur-
rounding medium, heat and mass diffusions are decoupled and are given by
Maxwell's equations (Maxwell, 1890):

$$\frac{dm}{dt} = \frac{4\pi(r+\Delta)DM}{RT} (P_\infty - P'_{r+\Delta}) \tag{2}$$

$$\frac{dm}{dt} = \frac{4\pi(r+\Delta)\kappa}{L} (T_\infty - T_r) . \tag{3}$$

D is the diffusion coefficient of vapor, κ is the thermal conductivity of the
medium, and L is the latent heat of vaporization. T_r is the surface tempera-
ture, and T_∞ and P_∞ are ambient temperature and pressure. Integrating the
Clausius-Clapeyron equation for small temperature differences gives

$$\frac{P'_r(T_r) - P'_r(T_\infty)}{P'_r(T_\infty)} \approx \frac{LM}{RT^2} (T_r - T_\infty) \ . \tag{4}$$

Combining Eqs. (3) and (4), we have

$$\frac{dm}{dt} = 4\pi r^2 \ \frac{\kappa T_\infty}{rL^2 \rho_{eq}(\infty)} \ \left\{ P'_r(T_r) - P'_r(T_\infty) \right\} \ , \tag{5}$$

where $\rho_{eq}(\infty) = \dfrac{P_r M}{RT_\infty}$ is the equilibrium vapor density of the ambient. Addition of Eqs. (1), (2), and (5) results in

$$\frac{dm}{dt} = \frac{RT}{M} \cdot \frac{P'_{r+\Delta}(T_r) - P_\infty}{\dfrac{r^2}{D(r+\Delta)} + \dfrac{bL}{\kappa} r + \dfrac{4}{\bar{v}\alpha}} \ , \tag{6}$$

where $\bar{v} = \sqrt{\dfrac{8RT}{\pi M}}$ is the velocity of the evaporating molecules. $b = \dfrac{L\rho_{eq}(\infty)}{RT^2}$ is the rate of change of the equilibrium vapor density with respect to temperature. The equilibrium vapor pressure over a droplet's surface depends on its curvature and the concentration of solute in the solution droplet and is given by

$$P'_{r+\Delta} = P_s \ \exp(\frac{2\sigma}{rR \ \rho_\ell T}) \cdot (1 - X_s) \ . \tag{7}$$

P_s is saturated vapor pressure, ρ_ℓ is density of the aerosol, σ is surface tension, and X_s is mole fraction of solute in the solution droplet.

Substituting for $P'_{r+\Delta}$ and denoting $S = P_\infty/P_s$ as the saturation ratio, and $R_i = 4/\bar{v}\alpha$, $R_m = r^2/D(r+\Delta)$, and $R_T = (bL/\kappa)r$ as the resistances to free molecule effusion, mass diffusion, and heat diffusion, Eq. (6) can be written as:

$$\frac{dr}{dt} = \frac{\rho_{eq}(\infty)}{\rho_\ell} \cdot \frac{S - (1 - X_s)\exp[2\sigma\rho_{eq}(\infty)/r\rho_\ell]}{R_i + R_m + R_T} \, . \tag{8}$$

Limiting Cases

For nonpolar liquids and polar liquids with short chain hydrocarbons, resistance in the interface is negligible, and evaporation is controlled by the rate of diffusion of water to the gas phase and diffusion of heat to the droplet. With a droplet large enough for Kelvin and solution effects to be neglected, Eq. (8) will reduce to

$$-\frac{dr^2}{dt} = 2\frac{\rho_{eq}}{\rho_\ell}\frac{1 - S}{\frac{1}{D} + \frac{bL}{\kappa}} \, , \tag{9}$$

as expected from Maxwell's equation.

Under these conditions, the lifetime of the droplet becomes

$$\frac{t_d D}{r_o^2} = \frac{1 + \frac{bLD}{\kappa}}{2\frac{\rho_{eq}}{\rho_\ell}(1 - S)} \, . \tag{10}$$

For submicron water droplets and for droplets containing a monolayer of surfactant film (small value of α), evaporation is kinetically rate controlled and $R_i \gg R_m + R_T$ (See Table 1.). Under these conditions Eq. (8) gives

$$-\frac{dr}{dt} = \frac{\rho_{eq}}{\rho_\ell}\frac{1 - S}{\frac{4}{\bar{v}\alpha}} \, , \tag{11}$$

the solution of which is

$$\frac{t_k \bar{v}\alpha}{r_o} = \frac{4}{\frac{\rho_{eq}}{\rho_\ell}(1 - S)} \, . \tag{12}$$

In the intermediate cases, the total lifetime of the droplet is

$$t_\ell = t_k + t_d .$$ (13)

Results and Discussion

The lifetimes of droplets undergoing evaporation have been calculated

using Eq. (8) and compared with limiting cases results given by Eqs. (10) and

(12). Figure 2 indicates the range of validity of each of the limiting cases.

When atmospheric fog droplets ($r_o \sim$ 1-5 μm) are covered with a surfactant film

with a moderate surface resistance, the error in using the kinetic model is

only a few percent. For larger droplets and flat surfaces, evaporation is

diffusion controlled. Kinetic effects become important only if the droplet is

covered by surfactants of long chain hydrocarbons with high film resistances.

The effects of relative humidity and temperature on the lifetime are seen in

Figs. 3 and 4. A strong dependence is observed at relative humidities of 80%

and higher. The lifetime is increased exponentially with a decrease in tem-

perature, primarily due to the changes in partial vapor pressure. These

graphs also show the dramatic effect of surfactant films on the fog stability.

Curvature Effect

The vapor pressure of the evaporating molecules over a droplet increases

over a flat surface by a factor expressed as the Kelvin coefficient. Assuming

$\dot{R}_r$ and $\dot{R}_\infty$ are the rate of evaporation for droplet and flat surfaces, we have

$$\varepsilon = \frac{\dot{R}_r - \dot{R}_\infty}{\dot{R}_r} = \frac{\exp(\frac{a}{r}) - 1}{\exp(\frac{a}{r}) - S} ,$$

where $a \simeq 10^{-3}$ $\overset{\circ}{A}$ for water evaporating at ambient conditions. For a droplet

1 μm in radius, the error in ignoring the Kelvin effect is less than 1% for

relative humidities of 90% or less.

Solution Effect

Reduction in the vapor pressure due to the presence of nonvolatile substances can retard the evaporation rate considerably. If the concentration is high enough, the evaporation can be stopped completely and the droplet can reach a new equilibrium state with its environment. If r* is the radius of the droplet at this new equilibrium state, we have:

$$\frac{dr}{dt}\bigg|_{r = r^*} = 0 \; ,$$

and

$$S = (1 - X_s)\exp[2\sigma\rho_{eq}(\infty)/r^*\rho_\ell] \tag{15}$$

Here $X_s = f\bar{M}_s$, where $\bar{M}_s$ is the molarity of the solute, and f is the pressure lowering factor which depends on the concentration, temperature, and nature of the solute (Int'l. Crit. Tables, 1926). Table 2 gives the equilibrium radius of the droplets of NaCl nuclei at different relative humidities.

Effect of Chemical Reactions

Absorption of gases and chemical reactions within the droplet can eventually reduce the surface vapor pressure to values smaller than equilibrium saturated vapor pressure, and therefore the droplet starts to grow again. This phenomenon can be particularly important when the critical radius is large enough to provide several layers of liquid water necessary for certain heterogeneous reactions to proceed. At the coast line, the salt nuclei may increase the critical droplet size and therefore facilitate heterogeneous chemical reactions and further droplet growth to sizes which attenuate light and thus reduce visibility.

As an example, we consider the catalytic oxidation of SO_2 on soot particles. Details of the reaction mechanism are given elsewhere (Chang, 1979). Oxidation is first order in carbon and zeroth order in SO_2 concentrations for pH > 5. Under these conditions,

$$\frac{d[SO_4^=]}{dt} \approx K(C_x)[O_2]^{.69} \qquad\qquad (16)$$

Here $K = 1.17 \times 10^5 \exp(-E/RT)$ moles$^{.31}$ $\ell^{.69}$/g·sec, with $E = 11.7$ kcal/mole, as determined for acetylene and natural gas soot. (C_x) is the concentration of graphitic carbon particles in g/m^3 of air, and $[O_2]$ is the concentration of dissolved oxygen in moles/ℓ. Figure 5 shows the result of such calculations. The solid curves represent the change in size over time of a droplet containing 10^{-13} gr of NaCl salt nuclei with a critical radius of 0.72 μm. Without the nuclei, the critical radius is .007 μm (dotted lines). For pure water or droplets covered with a weak surfactant (large α), the lifetime is short and the droplet evaporates before the sulfate production level is large enough to slow down evaporation. However, the presence of a monolayer of strong surfactants (α $\approx 10^{-6}$) will retard the rate of evaporation so that the sulfate concentration builds up and the droplet starts to grow again (broken lines in Fig. 5). The rate of growth is controlled by the concentration of carbon particles in the air (i.e., the reaction rate) rather than the initial nuclei concentration. Under these circumstances, the droplet lifetime is therefore limited to its fall time. The effect of pH is considered for more acidic environments (pH < 5) by using a new rate law (Chang, 1979); however, the pH effects are only of secondary importance and are not reported here.

Conclusion

In this paper we discussed the role of soluble and insoluble
matter in the stabilization of aerosol droplets. Soluble nuclei like sea salt
determine the equilibrium size of the droplet with the surrounding atmosphere.
If the nuclei are large enough to wet the aerosol, the adsorption of gases
followed by chemical reactions in the liquid phase instigate the growth of
the particle. Surfactants can reduce the evaporation rate by increasing the
interface resistances by several orders of magnitude. If the evaporation
coefficient is low enough, the evaporation rate can actually become smaller
than the rate of growth due to chemical reactions. Experiments are under way
to determine the evaporation coefficient and the nature of the surface films
of atmospheric aerosols from different origins.

Acknowledgment

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Table 1. Resistances for different droplet sizes at $T = 20°C$.

$r(\mu m)$	R_m $(\sec \cdot cm^{-1})$	R_T $(\sec \cdot cm^{-1})$	$R_i (\sec \cdot cm^{-1})$		
			$\alpha=10^{-2}$	$\alpha=10^{-4}$	$\alpha=10^{-6}$
0.1	1.8×10^{-5}	10^{-4}	6×10^{-3}	6×10^{-1}	60
1	3.9×10^{-4}	10^{-3}	''	''	''
10	4.4×10^{-3}	10^{-2}	''	''	''
100	4.4×10^{-2}	10^{-1}	''	''	''
1000	4.4×10^{-1}	1	''	''	''

Table II. Equilibrium radii of droplets of NaCl nuclei (microns).

	$m = 10^{-16}$ gr[a]	$m = 10^{-14}$ gr	$m = 10^{-12}$ gr	$m = 10^{-10}$ gr
S = .80	.043	.20	.93	4.3
S = .90	.053	.24	1.13	5.3
S = .95	.065	.30	1.40	6.5
S = .99	.111	.51	2.39	11.1

[a] m is nuclei mass.

Figure Captions

Figure 1. A schematic model of an evaporating droplet.

Figure 2. The dimensionless lifetime of a droplet covered with a film of surfactant. t_d and t_k are lifetimes at limiting cases of diffusion and kinetically controlled evaporation. t_ℓ is the calculated lifetime when both effects are considered. These graphs show the range of validity for each assumption.

Figure 3. The effect of relative humidity on the lifetime of a droplet at 20°C.

Figure 4. The lifetime of droplets as a function of temperature (S = .8).

Figure 5. The radius of an evaporating aerosol droplet in which oxidation reaction ($SO_2 \xrightarrow{C_x} SO_4^=$) occurs.

T = 10°C, S = .8, r_o = 5 μm, pH = 5.0

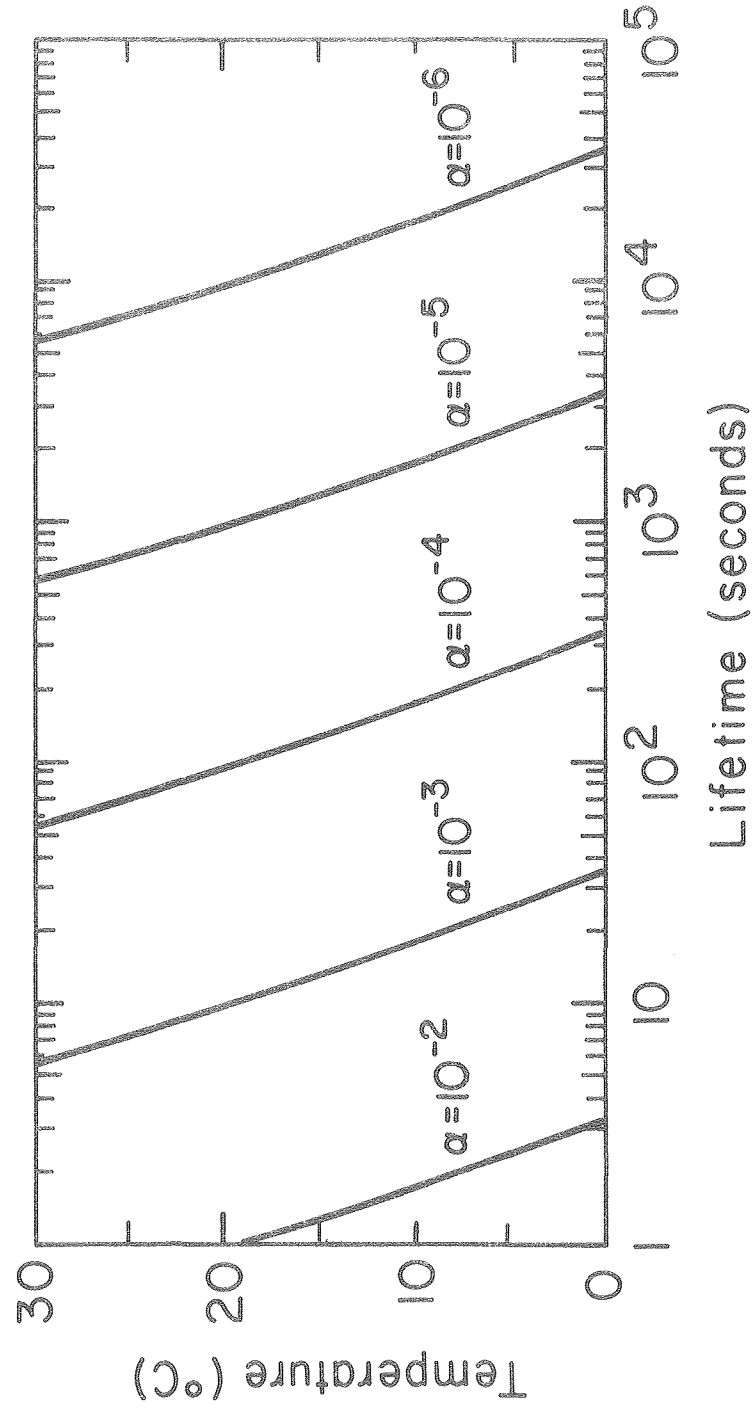· · · · · Pure water droplet (no catalyst, no chemical reaction)

——— Droplet containing 10^{-13} gr NaCl salt nuclei and insoluble carbon catalyst, no surface film (α = 1)

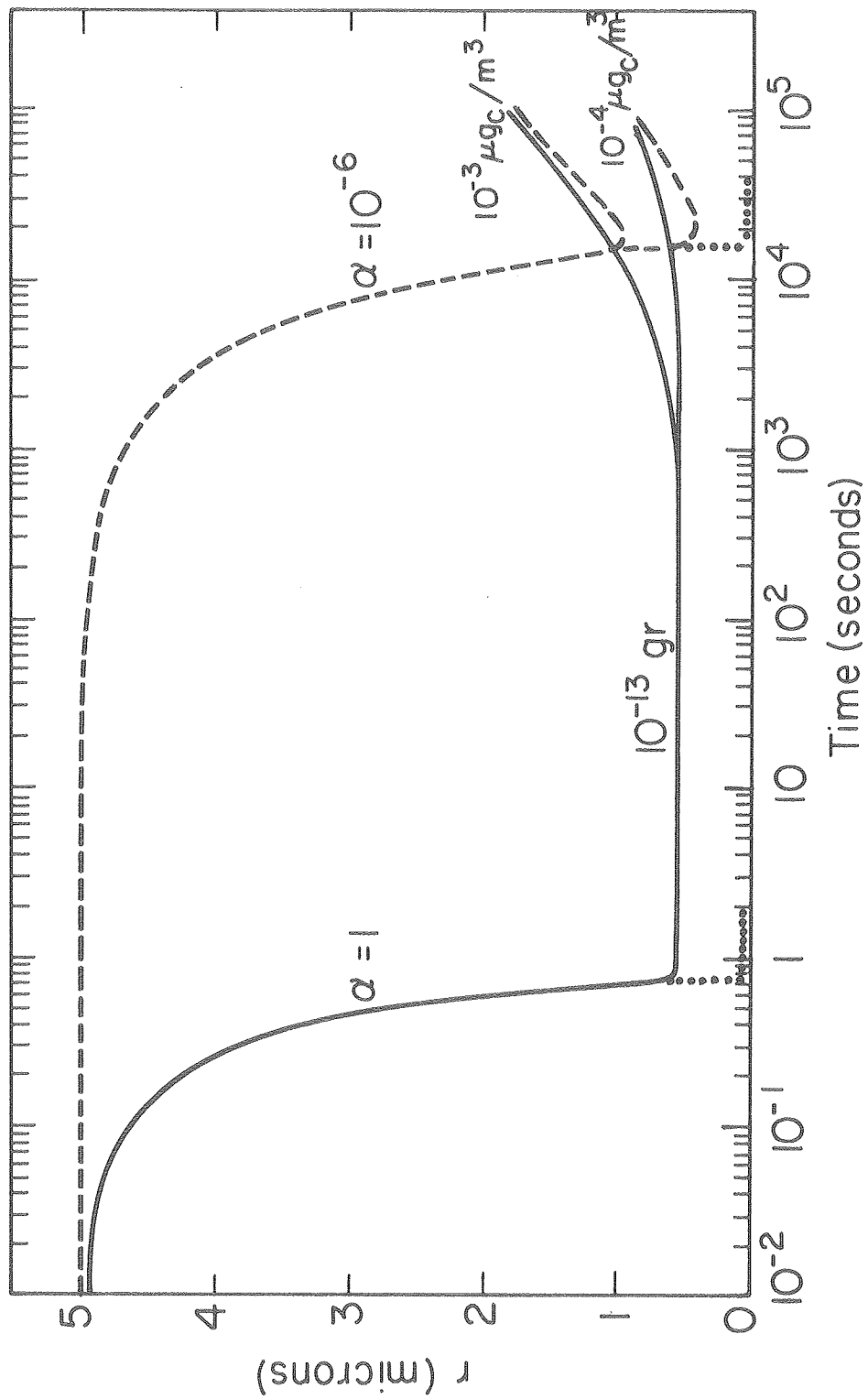– – – – Droplet containing only carbon catalyst and covered by a film of highly resistant surfactant (α = 10^{-6})
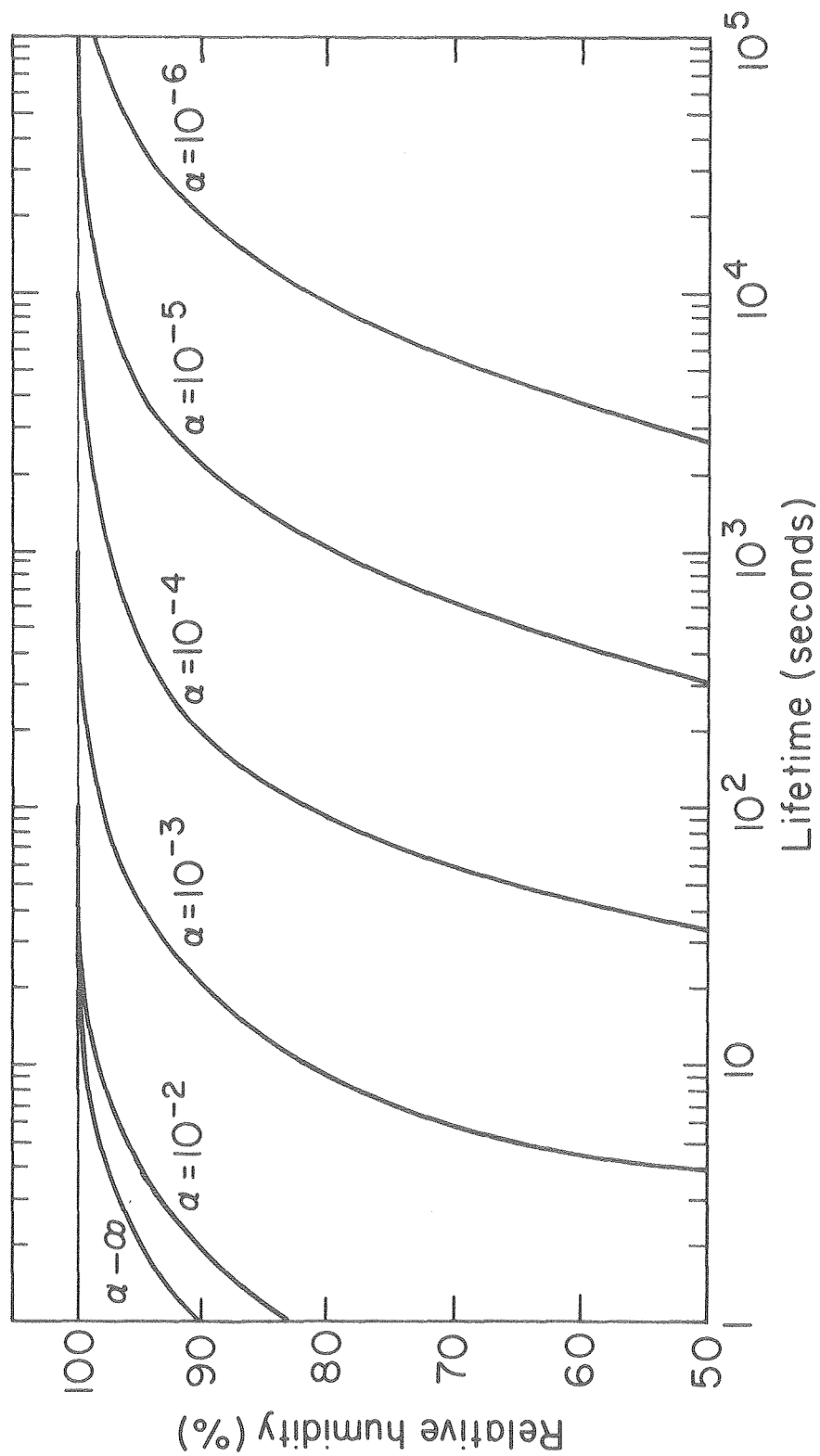
Figure 3.

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Figure 4.

Figure 5.